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The lower illustration is a comparison of a portion of the Kensington spectrum of Comet Brooks, and the Lick spectrum of Comet Daniel* (1907 *d*), the latter having been taken with a slit spectrograph. There can be little doubt that the two spectra are nearly identical, bunches of individual lines in the Lick spectrum being represented in the Kensington spectrum by wide and diffuse lines.

* 'Lick Bulletin,' No. 135.

*A Chemically Active Modification of Nitrogen, Produced by
the Electric Discharge.—III.**

By the Hon. R. J. STRUTT, F.R.S., Professor of Physics, Imperial College of
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§ 1. *Effect of Temperature on the Duration of Active Nitrogen.*

In the first paper (§ 2) it was mentioned that a stream of glowing nitrogen led through a tube cooled in liquid air glowed out with increased brilliancy, and then became extinguished. There is some ambiguity in the interpretation of this experiment, since the density of the gas is locally increased by cooling; and increased density may (and does) make the nitrogen expend its glowing power more quickly.

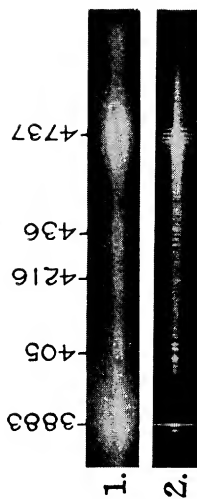
A hermetically sealed bulb containing rarefied nitrogen was excited by the electrodeless discharge. Allowed to expend itself at room temperature, the glow in this bulb was conspicuous for more than a minute. But if the bulb was immersed completely in liquid air immediately after excitation, and after 15 seconds withdrawn and examined, it was found to be quite dark. The glow was very brilliant as seen under the surface of the liquid air. This experiment proves that the glow-transformation really occurs more quickly the lower the temperature, apart from changes of density.

The same experiment was repeated, substituting boiling water for liquid air. Again the life of the glow was shortened, but this time its brilliancy

* Part I, 'Roy. Soc. Proc.,' 1911, A, vol. 85, p. 219; Part II, 'Roy. Soc. Proc.,' 1911, A, vol. 86, p. 56.



Spectra of Comet Brooks (1911 c). 1. September 30 ; 2. October 31.



1. Comet Brooks (1911 c), Kensington.
2. Comet Daniel (1907 d), Lick.

while it lasted was judged to be less than at ordinary temperatures. This corresponds very well with the results formerly obtained by the flow method. But now I feel able to offer more of an interpretation than was then possible. There are two phenomena to be reckoned with. One of these is a direct temperature effect on the glow-transformation. The other is a destructive effect of the walls of the vessel on the glow, also variable with temperature.

There are various reasons for believing in the existence of the latter effect:—

1. Certain substances, copper oxide, for instance, have been shown to be directly and immediately fatal to the glow, without themselves experiencing any change.* There is every probability that other solid surfaces, such as the glass walls, should, in a less degree, show the same effect.

2. When two similar glass bulbs are so thoroughly exhausted that no electrodeless discharge can pass, and then charged simultaneously with rarefied nitrogen and sealed off, the afterglow is about equally bright in each immediately after excitation. When a few seconds have elapsed, there is almost always a marked difference in luminosity between the bulbs. It is, in fact, impossible to get two bulbs which give the same rate of decay. As the initial intensity of glow is the same in each, this is most easily explained by supposing that the difference lies, not in the gas, but in the more unfavourable influence of the walls in the one case than in the other.

3. An experiment was made in which the glowing gas produced in one vessel was allowed to diffuse into two others, which were then shut off by a trap of sulphuric acid. The glow was initially of the same intensity in each vessel. The walls of one were wet with sulphuric acid, while those of the other were dry glass. The decay in the latter was much the more rapid. It cannot be doubted, therefore, that glass walls exercise some destructive action on the glow which sulphuric acid does not exert—at all events, in the same degree.

Admitting, then, that the walls produce a destructive effect on the active nitrogen analogous to that produced by cupric oxide, it is allowable to assume, as a working hypothesis, that this is increased by rise of temperature. The effect of cupric oxide, at all events, varies in that sense.

We are now in a position to interpret the observed effect of temperature on glowing nitrogen contained in a glass bulb. When cooled to $-180^{\circ}\text{C}.$, the effect of the walls in destroying the active nitrogen is, it is true, somewhat checked; on the other hand, the glow-transformation in the gas occurs more rapidly at that temperature, and the glow is given out in greater intensity and for a briefer period.

* 'Roy. Soc. Proc.,' 1911, A, vol. 85, p. 226.

When the bulb is heated to 100°C ., the destructive effect of the walls is increased, and this prevents the glow lasting so long as at ordinary temperatures, in spite of the fact that the glow-transformation is retarded. In the absence of the walls, the latter effect would make the glow feebler, but of increased duration. This, however, is not experimentally realisable.

We have it on the authority of Nernst* that no exception has been known to the rule that chemical change is accelerated by increase of temperature. The change from active towards inert nitrogen which is going on in the afterglow seems, therefore, to be unique in contradicting this rule.†

§ 2. *Effect of Density.*

Experiments on the duration of the glow with various densities of gas in the discharge vessel are difficult of interpretation, for two things are altered simultaneously—the conditions of discharge and the conditions of afterglow.

The effect of changed density can be examined to better advantage if the change is made when the gas is already glowing. The apparatus shown in fig. 1 was used to effect this.

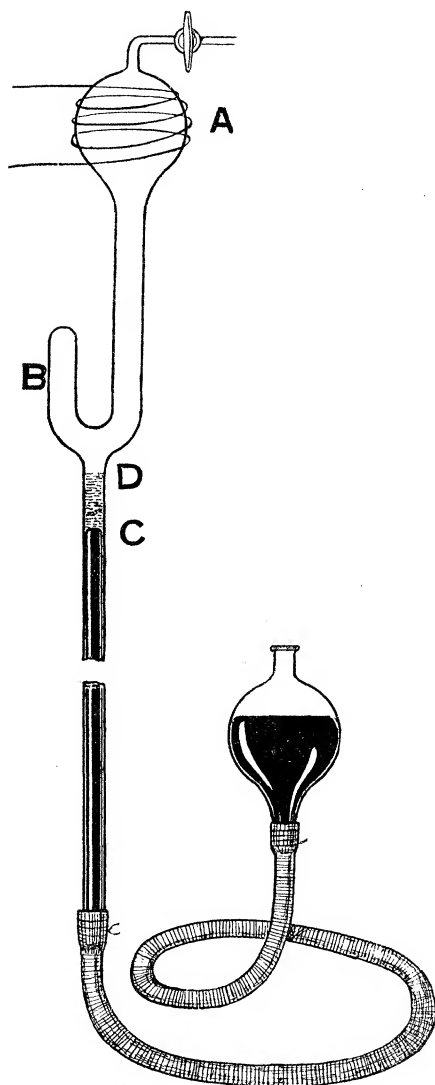


FIG. 1.

The electrodeless discharge passes in the vessel A. The afterglow diffuses almost immediately into the tube B. The mercury column C, covered with

* 'Theoretical Chemistry,' 1911 ed., p. 679.

† I desire to withdraw the too hasty suggestion made in Part I that the recombination of dissociated substances behaves in this way, and that this is a valid reason for regarding the active nitrogen as dissociated. It is necessary to distinguish between the effect of temperature in changing the rate of reaction and its effect in changing the condition of equilibrium to which the reaction tends (see Nernst, *passim*).

sulphuric acid* at D, can be raised so as to cut off the tube B from the rest of the vessel. The gas in B can be made to glow more brightly when compressed. In this condition it is more rapidly exhausted. If, after compression, the volume is kept constant, the glow gradually fades out. If it is *wholly* extinguished nothing is gained by compressing it further. But if any faint luminosity remains, it may be greatly increased by further compression. In this way the brilliance may be repeatedly restored by successive compressions. The process has been traced up to pressures of 4 cm. of mercury.

If, after compression to small bulk, the gas is again expanded, the luminosity is found to have disappeared, and tube B is now quite dark, though luminosity survives in the rest of the apparatus. If communication between B and A is again opened, a fresh supply of faintly luminous gas quickly diffuses in, and can be made to glow brightly by a second compression. This can be repeated several times without fresh excitation of the gas by discharge.

An alternative method of showing the effect of compression is more readily carried out, though less well adapted to a detailed study of the phenomena. In this case gas instead of liquid is admitted to drive the active nitrogen up to one end of the vessel.

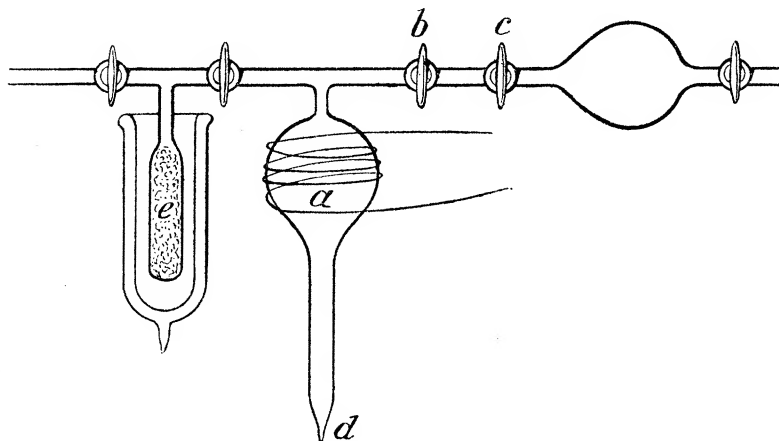


FIG. 2.

The electrodeless discharge passes in the vessel *a* (fig. 2), a bulb of 300 c.c. capacity. The afterglow is developed, and may be allowed to die down to a very low intensity. About 1 c.c. of nitrogen is then admitted

* When mercury was used uncovered, the glow was destroyed so soon as an attempt was made to compress it. This must be due to a destructive action of the mercury surface. I found formerly (*loc. cit.*, p. 225) that a mercury surface at rest had no effect on the glow. There must be some thin protective film on the surface of apparently clean mercury, which is broken up when it is moved.

from the space between the stopcocks *b* and *c*. This enters *a* and compresses the still glowing gas to the end *d*. A bright flash of luminosity is seen, due to the compression of the faintly glowing nitrogen already in the bulb.

To repeat the experiment, communication may be opened to the cooled charcoal in *e*, which quickly restores the degree of vacuum desired. The space between *b* and *c* is replenished from *f*.

The flash on compression is still more striking if *d* is immersed in an unsilvered vacuum vessel containing liquid air. In this way the intensity is increased by cooling as well as by compression.

In this form of experiment the nitrogen admitted merely acts as a piston compressing the glowing nitrogen, but not mixing appreciably with it. If the increase of pressure is made in such a way as not to cause a concentration of the glowing gas, no increased brightness is obtained. This may be realised in practice by gently admitting more nitrogen into a spherical bulb in which the glow has been generated, by means of a tube which projects into the centre, and is then provided with several jet-holes to distribute the entering gas uniformly in all directions.

The phenomena described are consistent with the following hypothesis:—Active nitrogen may revert to the normal condition in two ways—either by the action of the solid walls of the vessel, in which process no glow is emitted, or by its own spontaneous change, which is accompanied by the glow. This is analogous to what is known to happen in other gaseous reactions—the combination of oxygen and hydrogen, for instance. The change may be a volume one, with luminosity, as when the mixture is exploded; or it may occur at the surface of a solid catalyst, without luminosity, at comparatively low temperature.*

Although no quantitative measurements have been made, the experiments suggest that, with definite conditions of excitation, and if the effect of the walls could be eliminated, the time-integral of the intensity of the glow would be constant, unaffected by changes in temperature and density of the gas after excitation. The intensity of the glow is greatly dependent on these conditions, being increased by cooling or compression. But it is only increased at the expense of the duration.

§ 3. *Theoretical Inferences.*

It may be assumed that, where the action of the walls may be neglected, the visual intensity of the glow is a measure of the rate at which transformation is occurring. On this hypothesis, the compression phenomena described can give us valuable information as to the nature of the reaction from a

* See Bone and Wheeler 'Phil. Trans.,' 1906, A, vol. 206, p. 1.

molecular standpoint. If it is monomolecular, and the luminosity results from changes which can originate from a single molecule of modified nitrogen, then the rate of reaction will be proportional to the number of such systems in unit volume. The intrinsic luminosity should therefore increase on compression. But, if partial decay is allowed to occur at small volume, and the volume then restored, the amount of modified nitrogen remaining will be the same, and the glow will have the same brilliancy as it would have had after the same time interval, if no change of volume had been made at all. This is clear, without calculation, from the simple consideration that the transformation of each molecule of modified nitrogen is (on this hypothesis) independent, and that the number remaining after a given time cannot depend on whether the molecules have been brought close together or separated in the meanwhile.

We have seen, however, that this is *not* what is, in fact, observed. More rapid transformation occurs at high concentrations, and, on restoring the volume after considerable compression, the glow is found to have ceased, showing transformation to be nearly complete.

The observations, therefore, contradict the hypothesis of a monomolecular reaction. If we assume that the collision of two molecules of modified nitrogen is necessary to the reaction, then all is explained. Compression makes such collisions more frequent, and a given mass of modified nitrogen is more quickly transformed at small volume. The number of collisions is proportional to the square of the concentration; we may expect, therefore, very rapid increase of brightness when the volume is diminished beyond a certain point, by a piston moving with uniform velocity in a cylinder, as in the experimental arrangement. Since the active nitrogen is quickly used up at small volume, the luminosity will attain a maximum at a certain volume, the value of which depends on the velocity of the piston. On expansion after extreme compression, luminosity will be no longer visible.

The present experiments do not in themselves decide whether two or more than two molecules are concerned in the reaction. To do so, quantitative measurements of the law of decay would be necessary, and for this the action of the walls, which intervene in some way to cause a transformation without glow, would have to be eliminated. This action does not obscure the main features of the phenomenon, but it stands in the way of close quantitative scrutiny.

On general grounds, however, the reaction would naturally be regarded as bimolecular, in the absence of evidence that it is more complex.

§ 4. *Comparison with Prof. H. F. Newall's Experiments.*

Some very interesting experiments were described by Prof. H. F. Newall* in which he obtained brilliant luminosity from a sample of rarefied gas by compression after discharge. It was the study of his paper which led me to many of the above experiments, and any merit there may be in them must be largely credited to inspiration from this source. Prof. Newall was not able to specify precisely the nature of the gas with which his effect was obtained, or to reproduce it with certainty. He says: "I can only say that oxygen, with traces of nitrogen and SO_2 , is the mixture I should begin with, if I wished to recover the conditions" The spectrum given out on compression he identified with the negative glow spectrum of oxygen.

Prof. Newall kindly came to see my experiments, and, while agreeing that the effect was one of the same class as that which he discovered, was unable to admit their identity. He is confident that his gas gave an afterglow with continuous spectrum, and that a discontinuous one was only developed on compression.

It seems best to state what I feel to be a difficulty. In my experiments compression has the effect of making the gas give out *more quickly* radiation which it will give out in any case. This is in sharp contrast with Prof. Newall's view of his effect. Again, my effect only occurs in pure nitrogen. Prof. Newall's effect, if it is really analogous, and gives an oxygen spectrum, should occur in pure oxygen. Many careful experiments with oxygen spectroscopically pure have convinced me that it does not develop a band spectrum when compressed after discharge. The spectroscopic test of purity in the case of oxygen is a severe one, for oxygen lines are easily outshone by impurities.

I cannot help thinking that something of the following kind may account for Prof. Newall's result. Suppose that he had nitrogen with some oxygen to begin with—such a mixture would give an afterglow with continuous spectrum. Passing the discharge undoubtedly sometimes causes an absorption of oxygen in such cases, as I have myself seen,† and the nitrogen remaining would show the peculiar afterglow spectrum, which would shine out brightly on compression. It seems to me that this spectrum might easily be mistaken for the negative glow of oxygen, particularly as the observations had to be made quickly, and the nitrogen afterglow spectrum

* 'Camb. Phil. Soc. Proc.,' 1895, vol. 9, p. 295.

† This may be due to formation of oxides of nitrogen and their absorption by alkaline matter on or in the glass surface.

had not been described at the time. The bands of these spectra in the visual region are in the following positions:—

Oxygen negative glow	5985, 5870, 5592, 5248.
Nitrogen afterglow	6252, 5804, 5407, 5054.

Certainly no other known gaseous spectrum would give so close a general resemblance to the nitrogen afterglow spectrum.

It may be added that many attempts to produce Prof. Newall's effect with different gaseous mixtures containing oxygen have failed. There is, indeed, a brightening of the nitric oxide afterglow by compression to one end of the tube, but the spectrum remains continuous.

§ 5. *Summary.*

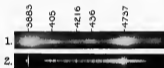
(1) Active nitrogen emits its energy more quickly, and reverts sooner to ordinary nitrogen, if it is cooled. This is apparently a unique instance of a chemical change accelerated by cooling.

(2) If the glowing gas is compressed to small volume, it flashes out with great brilliance, and exhausts itself in so doing. This proves that the glow-transformation is polymolecular, *i.e.* that more than one molecule must take part in it.

(3) Active nitrogen may revert to ordinary nitrogen in two distinct ways. One of those is a volume change, accompanied by glow, the other a surface action of the walls of the vessel, without glow. This is analogous to the behaviour of oxy-hydrogen gas in its transformation to water, which may be a surface or volume effect, according to circumstances.



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